

Optimization of the Cathode Long-Term Stability in Molten Carbonate Fuel Cells

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Objectives

- Improve the cathode stability.
- Develop a model for cathode performance.
- Increase the corrosion resistance and reduce the chromium leaching out of the stainless steel current collector in the MCFC cathode environment.

Key Milestones

- Reduced cathode dissolution was achieved by micro-encapsulation of cobalt on sintered nickel electrodes.
- Identified $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ as an alternate cathode material and its electrochemical performance was evaluated.
- Reduced chromium leaching-out was observed by coating Ni, Co and Ni-Co on SS current collector.
- Increased conductivity by cobalt-nickel electro-less deposition on current collector.
- Developed an agglomerate model, which was fit to the experimental data available in the literature.

Approach

Cathode: Different materials such as cobalt micro-encapsulated nickel electrodes, $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$, LiCoO_2 coated Ni, $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ coated Ni electrodes were prepared and used as alternate cathode material in MCFC. Half-cell performance studies were done in a 3-cm²-lab cell using identical electrodes as working and counter electrodes. The $(\text{Li}_{0.62}\text{K}_{0.38})_2\text{CO}_3$ eutectic embedded in a LiAlO_2 matrix was used as the electrolyte. Polarization studies were done using an oxidant gas composition of 70% air and 30% CO_2 . Two oxygen reference electrodes ($\text{Au}/\text{CO}_2/\text{O}_2$) connected to the electrolyte tile with a salt bridge ($50\%(\text{Li}_{0.62}\text{K}_{0.38})_2\text{CO}_3 + 50\%\text{LiAlO}_2$) were used to monitor the polarization of cathode. Electrochemical impedance spectroscopic studies were performed using a Model 1255 Schlumberger Frequency Analyzer. The electrode was stable during the experiments and its open circuit potential changed less than 1 mV. The impedance data generally covered a frequency range of 1-mHz to 100-kHz. A sinusoidal AC voltage signal varying by ± 5 mV was applied in all cases.

Model Development: Research in MCFC has been directed to improve cathode material and through-synthesis of alternate materials or surface modification of existing cathodes. Alternate cathodes, such as LiCoO_2 and LiFeO_2 , have been used to avoid the dissolution problems faced with NiO. However, these materials suffer from lower reaction kinetics and/or higher ohmic resistance compared to Nickel oxide. The search for alternate cathode materials could be simplified through the use of theoretical models, which simulate the performance of the MCFC cathode under a wide range of operating conditions. It is also desirable to study the influence of various electrode design parameters on the polarization behavior of the MCFC cathode. Agglomerate model [1] has been widely used to study the performance of the cathode in MCFC. The principal deficiency of the agglomerate model, apart from the simplified pore structure assumed, is the lack of measured values for film thickness and agglomerate

radius. Both these parameters cannot be estimated appropriately. The agglomerate radius can be estimated from post-test SEM micrographs. However, this radius is not the same along the whole length of the electrode. Further, as discussed by Prins Jansen et al. [2] attempts to estimate the thickness of the film vary by two orders of magnitude. Also, using the agglomerate model it is not possible to determine potential/current variations in directions perpendicular to the depth of the electrode. A pseudo-2D model was used by Fontes et al. [3] to determine the effect of different design parameters on the performance of the MCFC cathode. In this approach the local reaction rate was solved separately using the agglomerate approach. This was input as a source function in solving for the potential/current variations in two dimensions. This approach does not convey the true physical picture and is still limited due to the de-coupling of the potential from the reaction rate and the use of the agglomerate radius.

The above problems associated with the agglomerate model can be avoided if we take the alternate approach, namely the volume averaging technique [4,5]. As compared to the agglomerate model, where macropores and micropores remain as separate entities, in this approach, the pores in the electrode exist in a single continuum. Further, all three phases co-exist within the porous electrode and reaction proceeds everywhere at the solid/melt interface. Using the volume averaging technique, Prins-Jansen *et al.* [4] developed an impedance model for extracting the reaction and transport parameters from experimental data. Model simulations were fitted to experimental data within a certain confidence interval. They found that the diffusion coefficient of O_2 and CO_2 is three orders of magnitude larger than that estimated from the agglomerate model. Other parameters were of the same magnitude as reported by Lee et al. [6].

The model developed by Prins-Jansen et al. [4] combines both the electrolyte and gas phases into a single entity during volume averaging. The gas and liquid phase mass transport were not considered separately. Here, we will adopt the volume averaging technique as outlined by De Vidts and White [5] for three phase reactions in porous electrodes. Using this approach, volume averaged concentrations of both gaseous and liquid phase reactants are obtained separately. Apart from this, there also exists a need for developing a

comprehensive full cell model of the molten carbonate fuel cell. Present models in the literature are no more than a set of empirical equations, which are valid only for specific experimental conditions for which they were derived. Apart from analyzing the performance, the fuel cell model should also help in material selection and optimizing the design of different cell components.

Current Collector Studies: Austenitic steels are typically used for the construction of cathode current collectors and separator plates in molten carbonate fuel cells. Under normal operation and cathode atmosphere, the current collector becomes oxidized forming a porous corrosion scale. Dissolution and reaction of chromium with the electrolyte also occurs. As a consequence, electrolyte is consumed and the current collector loses its properties. Two different approaches have been taken in order to improve the properties of the current collector. First, the surface modification of stainless steel by administering a protective coating, which will possess good conductivity and better corrosion properties. Second, the evaluation of a different alloy that could be used as a current collector in the cathode side of the MCFC.

For the first approach, electrodes of area 1 cm^2 were made from a perforated SS304. The electrodes were cleaned before the characterization studies. Co-Ni encapsulation on SS304 electrodes was carried out using a procedure developed in our laboratories [7]. The solubility of the corrosion products was determined by immersion tests in molten carbonate under cathode gas conditions. Samples were taken every 6 hours. The molten carbonate sample was dissolved in 10% dilute acetic acid. Atomic absorption spectroscopy was used to analyze the concentration of dissolved nickel and chromium concentrations. The *in-situ* oxidation of bare and surface modified SS 304 electrodes were studied using a three-electrode set-up. The open circuit potential and cyclic voltametric studies were performed. Impedance analysis and I-V polarization studies were performed using a 3 cm^2 lab scale half-cell. The corrosion studies were carried out by using SS304 plates on both sides of the separator. $LiAlO_2$ separator containing $(Li_{0.62}K_{0.38})_2CO_3$ was used as the separator matrix. Oxidant gas with a composition of 30% CO_2 and 70% air was passed on both ends. A gold reference electrode with a reference gas of 66% CO_2 and 33% O_2 was connected through a salt bridge. A scanning

electron microscope, energy dispersive spectroscopy, and x-ray diffraction were used to study the microstructure and composition of the corrosion products.

Results

Cathode: The short-term stability of cobalt micro-encapsulated nickel electrodes, $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$, LiCoO_2 coated Ni, $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ coated Ni electrodes were studied using pot tests. Atomic absorption (AA) was used to analyze the dissolved nickel in the melt. Figure 1 shows the results of AA analysis on the amount of dissolved nickel in the carbonate melt as a function of time. The results indicate that cobalt doping increases the resistivity of the oxide to the molten carbonate environment. The amount of nickel cation in the carbonate melt increases with time and saturates after about 100 hours. The dissolution rate obtained for $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ is about one half of the dissolution of state-of-the-art nickel oxide reported in literature [8-10].

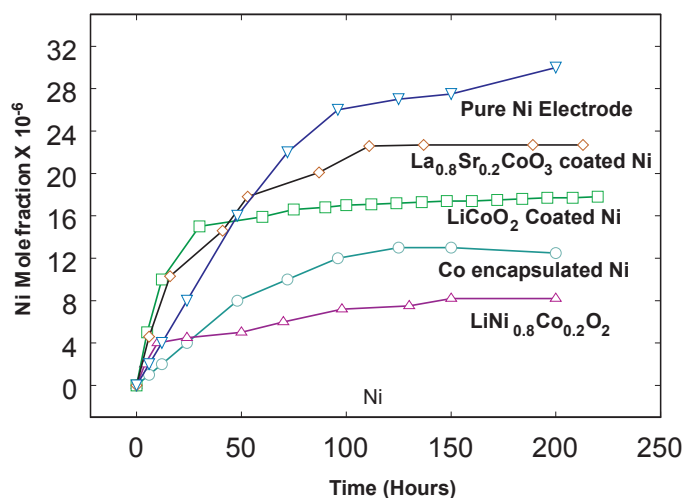


Figure 1. Solubility values of different cathode materials used in MCFCs.

Model Development: This model based on volume averaging was used in studying the effect of different parameters on the performance of the cathode, optimizing the thickness of the cathode for maximum performance, and in studying the effect of different gas compositions on cathode performance. The model was fit to experimental data at different temperature. Figure 2 compares the model to our experimental data of LiNiCoO_2 at different temperatures. With increase in temperature the reaction rate as given by the exchange

current density and the species transport rate as given by the diffusion coefficient increase. Further the electrolyte conductivity also increases. This fitting was used to find the dependence of different parameters on temperature. Figure 3 shows the model fit to experimental data for different cathode catalysts to extract the kinetic and conductivity parameters of the different materials.

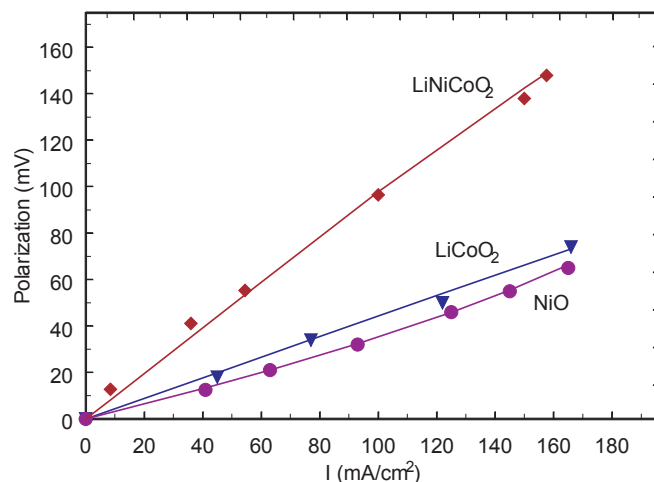


Figure 2. Comparison of the model to experimental data of LiNiCoO_2 at different temperatures

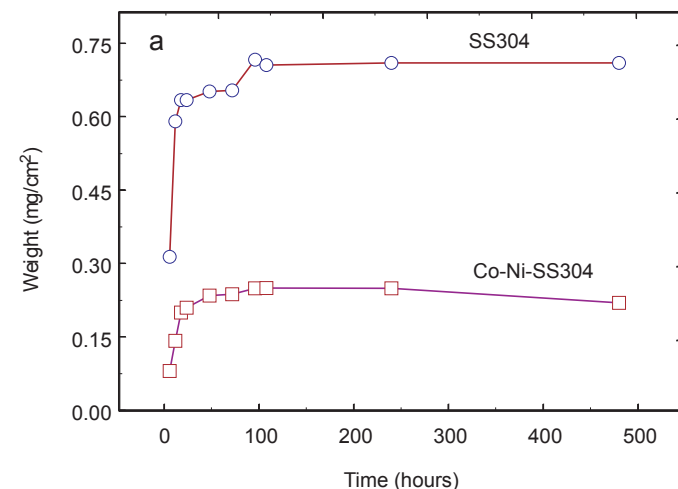


Figure 3. Comparison of polarization loss of different cathode materials.

The values are shown in Table 2. After optimizing the performance of the cathode, a comprehensive model for the full molten carbonate fuel cell was developed, based on the same volume averaging approach. The full cell model was used to study the losses associated with each of the cell components and to analyze the importance of various electrode parameters in determining cell performance. The importance of mass transfer effects was analyzed. The maximum power density was determined as a function of the cell thickness. Finally the model was fit to experimental data available in the literature.

Current Collector Studies: Short-term stability of the corrosion products formed in case of SS304 and Co-Ni encapsulated SS304 in molten carbonate eutectic were determined using immersion tests. Atomic absorption spectroscopy (AAS) was used to analyze the dissolved chromium and nickel in the melt. Figure 2 shows the results of AAS analysis for the dissolved chromium in the carbonate melt as a function of time. As shown in Figure 4, the concentration of chromium in the melt was higher in the case of bare SS304, when compared to that of Co-Ni encapsulated SS304.

It has been reported in the literature that SS304 forms a corrosion layer under cathode conditions consisting of LiFe_5O_8 [11]. EDAX analysis indicates a decrease of the chromium concentration in the surface. The cobalt and nickel contents did not change appreciably during the cell operation indicating a very stable coating. Impedance curves were analyzed by comparing the curves with those of a plausible electrical circuit to extract parameters (circuit elements) that can be related to physical processes, which are believed likely to be present. To compensate for this deviation from reality, a distributed phase element was added to the equivalent circuit. The parameter conductivity of the porous electrode, R_1 , and polarization resistance, R_2 , which are extracted from the impedance response using the equivalent circuit model, is summarized in Table 1.

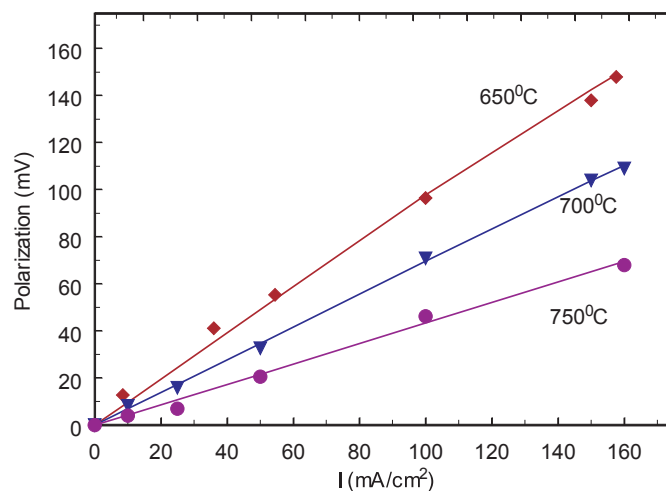


Figure 4. Chromium dissolution from bare and Co-Ni coated SS 304.

Table 1. Resistance Values Obtained from EIS Equivalent Fit

| EIS Equivalent Circuit Fit | | |
|----------------------------|--|--------------------------------------|
| Current Collector | Porous electrode Ohmic Resistance (Ω) | Polarization Resistance (Ω) |
| SS304 | ~5.3 | 120.68 |
| Co-Ni-SS304 | ~1.3 | 22.86 |

Table 2. Kinetic and Conductivity Properties for Different Cathode Materials

| Cathode material | σ (S/cm) | i_o (mA/cm²) |
|--------------------|-----------------|----------------|
| NiO | 13 | 50 |
| LiCoO_2 | 1 | 5 |
| LiNiCoO_2 | 5 | 0.65 |

Conclusions

Cathode: Cobalt coated electrodes have a lower solubility in the molten carbonate melt compared to bare nickel electrodes in the presence of cathode gas conditions. The solubility decreased more than 50% due to micro encapsulation with cobalt. The cobalt encapsulated nickel electrode showed a polarization of 95 mV for an applied current density of 160 mA/cm². The LiNi_{0.8}Co_{0.2}O₂ shows a lower rate of dissolution in molten carbonate under cathode gas conditions when compared to that of NiO. The i-V characteristics of LiNi_{0.8}Co_{0.2}O₂ are good, offering a current drain of 160 mA/cm² for a voltage polarization (IR free) of 140 mV.

Model Development: The electrolyte conductivity and exchange current density have very large effect on the performance of MCFC cathode as compared to other parameters. Due to low electrolyte conductivity, as compared to solid phase conductivity, most of the polarization loss occurs in a region close to the electrolyte matrix. Most of the material within the center of the electrode does not take part in the electrochemical reaction. This leads to low active material utilization within the electrode. Both low electrode and electrolytic conductivity lead to very poor reaction rate distribution across the electrode.

Current Collector Studies: The immersion tests we conducted on SS304 and Co-Ni encapsulated SS304 indicated higher chromium and nickel dissolution rate in the case of SS304, when compared to Co-Ni encapsulated SS304. SEM and EDAX analysis of the post-test SS304 indicated a loss of Cr from the surface. The surface composition of Co-Ni-SS304 showed very little change in terms of Co and Ni content, suggesting that the corrosion scale predominantly consists of Co and Ni oxides. XRD patterns of the corrosion scales indicated the presence of lithium ferrite, along with LiFe₅O₈ in the case of SS304 and mixed lithium-cobalt-nickel-iron oxides in the case of Co-Ni-SS304. Conductivity of the corrosion scale was higher in the case of Co-Ni encapsulated SS304 when compared to bare SS304.

References

1. C. Y. Yuh, and J. R. Selman, *J. Electrochem. Soc.*, **131**, 2062, (1984).
2. J. A. Prins-Jansen, K. Hemmes, and J. H. W. de Wit, *Electrochem. Acta*, **40**, 3585, (1997).
3. E. Fontes, M. Fontes, and D. Simonsson, *Electrochem. Acta*, **41**, 1, (1996).
4. J. A. Prins-Jansen, J. D. Fehribach, K. Hemmes, and J. H. W. de Wit, *J. Electrochem. Soc.*, **143**, 1617, (1996).
5. P. De Vidts, and R. E. White, *J. Electrochem. Soc.*, **144**, 1343, (1997).
6. G. L. Lee, J. R. Selman, and L. Pomp, *J. Electrochem. Soc.*, **140**, 390, (1993).
7. A. Durairajan, B. Haran, B. Popov, and R. E. White, *Journal of Power Sources*, submitted for publication, (2002).
8. K. Tanimoto, Y. Miyazaki, M. Yanagida, S. Tanase, T. Kojima, N. Ohtori, H. Okuyama, T. Kodama, *Denki Kagaku*, **59**, (7), 619, (1991).
9. K. Ota, S. Mitsushima, S. Katao, S. Asano, H. Yoshitake, and N. Kamiya, *J. Electrochem. Soc.*, **139**, (3), 667, (1992).
10. X. Zhang, P. Capobianco, A. Torazza, and B. Passalacqua, *Electrochemistry*, **67**, (6), (1999).
11. M. Keijzer, Ph.D. Thesis, Delft University, Netherlands, (1998).